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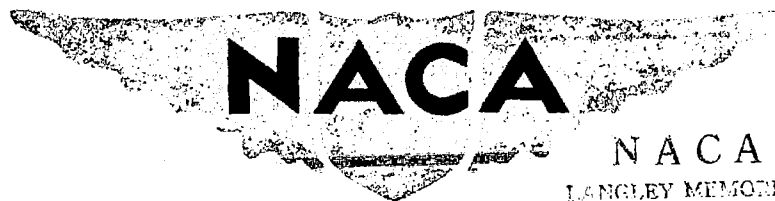
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QUANTITATIVE ANALYSIS FOR AROMATIC AMINES IN AVIATION
FUELS BY ULTRAVIOLET SPECTROPHOTOMETRY

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

ADVANCE RESTRICTED REPORT

QUANTITATIVE ANALYSIS FOR AROMATIC AMINES IN AVIATION
FUELS BY ULTRAVIOLET SPECTROPHOTOMETRY

By Adelbert O. Tischler

SUMMARY

A method of quantitative analysis for individual aromatic amines or mixtures of aromatic amines in hydrocarbon fuel blends by spectrophotometric measurement of ultraviolet-light absorption is presented. The effect of the precision of the spectrophotometric measurements, the purity of the aromatic amine, photochemical decomposition of the amine, and the composition of the fuel on the accuracy of the analysis is discussed and the results of tests of the precision of the procedure are given.

The accuracy of the spectrophotometric method depends upon the purity of a standard sample used for calibration purposes, as well as the extent of contamination of the fuel with other substances which absorb ultraviolet light in the region from 3050 to 2800 Å wavelength and which can be extracted from the fuel by aqueous hydrochloric acid along with the amine. The analysis is not affected by the type of hydrocarbon in the gasoline, nor do tetraethyl lead or ethyl-fluid dye in the amounts usually present in aviation fuels interfere. In analyses of typical hydrocarbon and gasoline solutions containing various aromatic amines in concentrations from 0.4 to 1.7 percent by weight, results accurate, on the average, within 1/2 percent of the amine have been obtained.

INTRODUCTION

The need for large quantities of aviation gasoline of high antiknock rating led to the limited use of blends containing up to 3 percent of aromatic amines in fuels for military aircraft. Because a number of different aromatic amines and their mixtures have been considered for this purpose, it has been necessary to develop methods of quantitative analysis for various amines in gasoline.

In the past, chemical methods of analysis have been used, the most practical of which were based on titration of the amine with an acid. According to reference 1, titration with aqueous hydrochloric acid is not entirely satisfactory because the gasoline composition, particularly if aromatics are present, affects the results and tertiary amines, such as N,N-dimethylaniline, cannot be determined. In general, methods employing titration have been somewhat limited in scope and the accuracy has not been better than about 1 percent of the amount of amine present.

Spectrometric measurements of the ultraviolet-light absorption of aromatic amines have been used at the NACA Cleveland laboratory for about 2 years to determine the concentration of aromatic amines in aviation fuel blends. The spectrometric method is more accurate than the titration methods and has proved to be applicable to the quantitative determination in hydrocarbon solutions of all monoaryl amines tested at this laboratory. Quantitative analysis of technical xylidines in gasoline by spectrophotometry has been reported by the Technical Advisory Committee of the Petroleum Industry War Council (reference 2).

This report describes an ultraviolet spectrochemical method of quantitative analysis for individual aromatic amines (or for mixtures of amines) in amine-fuel blends. Factors that affect the analysis are discussed and data are presented to show the precision of the method for several typical types of analysis made with a photoelectric spectrophotometer having 1-centimeter absorption cells (reference 3). Absorption spectra obtained with this instrument are given in reference 4 for 27 aromatic amines in isooctane and in water together with a discussion of some factors which have been found to affect the absorption characteristics of the amines. A discussion of qualitative analysis is not attempted in the present paper and it is assumed throughout that the identity of the aromatic amine or aromatic amine mixture is known.

PRINCIPLES OF SPECTROPHOTOMETRIC DETERMINATION OF AROMATIC AMINES

Monoaryl amines absorb ultraviolet light of wavelengths from about 3100 Å to less than 2000 Å and have a characteristic absorption band at about 2900 Å. Although the absorption spectra of individual aromatic amines in hydrocarbon solutions differ somewhat, the selective absorption of ultraviolet light of about 2900 Å wavelength is distinctive of aromatic amines in gasoline. Aromatic and olefinic hydrocarbons have their principle absorption at shorter wavelengths although weak absorption at 2900 Å is possible, whereas paraffinic and naphthenic hydrocarbons are transparent to near-ultraviolet light. Aromatic amines absorb ultraviolet light at 2900 Å sufficiently to facilitate the detection of concentrations as small as 10^{-5} percent in ultraviolet-light-transparent solvents.

The absorption of ultraviolet light by aromatic amines does not preclude the spectrometric determination of aromatics in fuel blends (reference 5) because the amine can be selectively removed from the hydrocarbon solution with aqueous acids. The chemical reactivity of aromatic amines with aqueous acids also permits the elimination of possible interference in the amine analyses by aromatics or unsaturated hydrocarbons. A detailed discussion of the principles of eliminating interference by aromatic and olefinic hydrocarbons is given in appendix A.

The determination of an individual aromatic amine in a fuel sample is based on the following procedure:

1. A measured portion of the fuel sample containing the aromatic amine is diluted quantitatively with an ultraviolet-light-transparent hydrocarbon solvent to a concentration for which the light absorption by the amine is measurable.
2. The aromatic amine is extracted with hydrochloric acid from a portion of the diluted sample.
3. The difference in ultraviolet-light absorption between the unextracted and the extracted hydrocarbon solution is measured spectrophotometrically.
4. The net ultraviolet-light absorption of the sample is compared with that of a standard solution containing a known amount of the aromatic amine and the concentration of the unknown sample calculated. The Beer-Lambert law is assumed to be valid.

It is apparent that the concentration of a mixture of aromatic amines in a fuel sample can be determined in a similar manner, providing that a sample of the amine mixture can be obtained for determining the absorption of a standard solution.

ANALYTICAL PROCEDURE

For spectrophotometric measurement of the light absorption of the aromatic amine, the fuel sample is diluted with isooctane to a concentration of approximately 0.03 gram of aromatic amine per liter of isooctane (approximately 0.004 percent by weight). This concentration yields absorption measurements in the optimum range from 0.4 to 0.7 in extinction (40 to 20 percent light transmission) for most monoaryl amines boiling below 250° C. Throughout this paper the values of light absorption are expressed in terms of extinction rather than as percentage of light transmission because the extinction is proportional to the concentration of the absorbing solute

when the Beer-Lambert law holds. The extinction is the negative logarithm of the ratio of light intensity transmitted through the solution cell to that transmitted through a matched cell containing the solvent.

The specific extinctions for the particular amine or known amine mixture in the fuel blend must be determined before the amine in the fuel can be determined quantitatively. (See step 4 of procedure outlined in preceding section.) At a particular wavelength the specific extinction is a proportionality factor that relates the extinction of the aromatic amine solution for a cell of unit length with the concentration of the aromatic amine; the factor is obtained from measurements of the ultraviolet-light absorption of a fuel sample that contains a known concentration of the aromatic amine to be determined.

A commercial grade of isooctane (known as S reference fuel) has been found suitable for dilution of the samples for routine analysis. Isooctane that is not sufficiently transparent to ultraviolet light may be purified by a procedure described in reference 6.

Determination of Specific Extinctions of the Standard Aromatic Amine Solution

A weighed amount of the aromatic amine (or aromatic amine mixture) to be determined is dissolved in a weighed amount of fuel to prepare an amine-fuel blend of known concentration approximately equal to that of the aromatic amine in the fuel samples to be analyzed. For maximum accuracy it is preferable to dissolve the amine in a fuel similar in composition to the fuel samples to be analyzed. A weighed portion of the prepared amine-fuel blend is then diluted to a specific volume with isooctane until the final solution of at least 100 milliliters has a concentration of aromatic amines of about 0.03 gram per liter of isooctane solution. In order to conserve solvent, the final dilution in isooctane is obtained by a series of two dilutions.

About 50 milliliters of the isooctane solution are transferred into a 250-milliliter separatory funnel having an ungreased stopcock. (Solution of grease by the fuel may vitiate the analyses.) The aromatic amines are extracted with 5 milliliters of 1:1 hydrochloric acid by agitating the liquids in the separatory funnel for 2 minutes. The hydrochloric-acid layer is then separated from the isooctane solution and the acid remaining in the isooctane layer is removed by washing with 5 milliliters of distilled water.

After the water has settled out of the isooctane solution, one of the cells of the spectrophotometer is filled with a portion of the extracted isooctane solution. A second cell is filled with a portion of the unextracted part of the isooctane solution. The extinctions E of the solution in the second cell are measured relative to the solution in the first cell at three wavelengths spaced at intervals of approximately 25 Å over the peak of absorption in the region of 2900 Å for the particular amine (or amine mixture) being determined (see appendix B).

The specific extinction k of the aromatic amine at each wavelength is calculated from the equation

$$k_{\lambda} = \frac{E_{\lambda} V}{c l W}$$

where

- k_{λ} specific extinction at wavelength λ expressed as liters per gram-centimeter
- E_{λ} measured extinction at wavelength λ for unextracted isooctane solution relative to extracted isooctane solution
- c concentration of aromatic amine in original amine-fuel blend, grams per gram
- l length of absorption cells, centimeters
- W weight of original amine-fuel blend taken, grams
- V volume to which W is diluted in final isooctane solution, liters

Analysis of Fuel for Aromatic Amine Content

A sample of the fuel to be analyzed is weighed and diluted volumetrically with isooctane to a concentration of the known aromatic amine of about 0.03 gram per liter. Adjustment of the sample solution to the appropriate amine concentration may require preliminary trial dilutions. Part of the diluted sample is extracted with aqueous hydrochloric acid and the extinctions of the unextracted portion, relative to the portion from which the amine has been extracted, are measured at the wavelengths previously used for the standard sample.

The concentration of the aromatic amine in the original fuel sample is calculated from each measured extinction using the equation:

$$c = \frac{E_{\lambda} V}{k_{\lambda} l W}$$

where E_{λ} , V , and W here refer to the analysis of the unknown sample.

Three values of c can be calculated from the extinctions at the three different wavelengths. The three values are averaged to obtain the result of the analysis. For more precise analyses, the extinctions for both unknown and standard samples can be measured at a greater number of wavelengths and the results of independent analyses can be averaged.

The calculations in the foregoing procedure yield the weight fraction of aromatic amine in the fuel. Results may also be obtained on a volume-percentage basis provided that consistent sets of measurements and units are employed in the calculations.

FACTORS THAT MAY AFFECT ANALYSES

Precision of Spectrophotometric

Measurement of Extinction

Relation between extinction and concentration of amine. - In the calculations given in the Analytical Procedure, the Beer-Lambert law is assumed to hold. Although this assumption is generally valid for absorption of monochromatic radiation, most ultraviolet spectrophotometers transmit wavebands from 20 to 100 Å and the relation between extinction and aromatic amine concentration should be verified. For the spectrophotometer used at this laboratory the extinction readings of several dilutions of a solution of technical xylidines in isooctane, measured at 2925, 2900, and 2875 Å, were found to be proportional to the concentrations of the aromatic amine mixture for extinction values up to about 1.0. Values of the specific extinctions of the technical xylidines, calculated from the measured extinctions, agreed within an average deviation of less than 1/4 percent. The results are tabulated in table 1.

Choice of wavelengths and spectrophotometer slit widths. - The extinctions determined for each aromatic amine will depend upon the wavelengths and the slit widths used and the absorption-cell lengths.

In general, the wavelengths used for quantitative analysis of individual aromatic amines lie near the peak of the 2900 Å absorption band for the particular amine. The effects of small errors in wavelength setting on the results are usually negligible for absorption spectra showing broad continuous bands, particularly at or near an absorption maximum. For the spectrophotometer used this source of error was negligible relative to other sources of uncertainty in the analyses for aromatic amines.

For the analysis of the aromatic amines, changing the spectrophotometer slit widths from 0.3 to 0.5 millimeter was found to have no significant effect on the measured extinctions except for amines having complex absorption spectra, namely, aniline and the p-alkylanilines. Slit widths of 0.3 millimeter were ordinarily used for the analyses.

Absorption cells. - "Matched" quartz absorption cells seldom match exactly, either in optical length or in absorption by the quartz windows. Errors greater than 1/2 percent may result if these factors are ignored.

For the analysis of typical aviation fuels by the method described, the error in the analysis caused by the use of cells differing in length by 1 percent is estimated to be 1/2 percent. The error is minimized in the case of aromatic amine solutions which have no other substances that absorb ultraviolet light at the wavelengths used for the analysis.

The corrections for differences in absorption by the quartz windows of the absorption cell are obtained after carefully cleaning the cells with ethyl alcohol. Both cells are then filled with the isooctane solvent, and the extinction of the solution cell is measured relative to the reference cell. The extinction correction for the solution cell at each wavelength is subtracted algebraically from the extinction of each solution measured in that cell.

Purity of the Aromatic Amine

Because the method of analysis is based on a comparison of the absorption of an amine in the unknown sample with the absorption of the amine dissolved in a standard hydrocarbon solution, the absolute accuracy of the determination is dependent upon (1) the absolute purity of the amine used in preparing the standard amine-fuel blend and (2) the purity of the amine in the fuel being analyzed. Obviously, any impurity that alters the absorption spectrum of the amine in the fuel or the amine used for the standard amine-fuel

blend will affect the results. For example, suppose the fuel blender adds to a gasoline an aromatic amine which is 99 percent pure and which contains as an impurity 1 percent of a different aromatic amine with twice the specific extinction of the amine added. In the analysis, the measured extinctions will then be 1 percent higher than if the amine had been absolutely pure. Suppose also that the analyst obtains a sample of the aromatic amine which is only 97 percent pure and which contains 3 percent of aromatic hydrocarbons that absorb relatively weakly at the wavelengths used for analysis of the aromatic amine. The specific extinctions determined for the amine will be nearly 3 percent lower than they would be for the pure amine. The resultant analysis of the aromatic amine in the blended fuel will be about 4 percent higher than it should be because of these cumulative error factors. Thus it is evident that the purity of the amines analyzed and particularly of the amine used for a standard is an important factor in establishing the accuracy of the analysis. On the other hand, if the analyst receives from the fuel blender a sample of the amine added to the fuel, he may then analyze the fuel in terms of the added aromatic amine with an accuracy limited primarily by the precision of the analytical technique, even though the results are not necessarily correct in terms of a pure amine.

The most common impurities in an aromatic amine are isomers of the amine. The presence of considerable amounts of isomeric aromatic amines, which usually have similar absorption spectra (reference 3), can often be tolerated without seriously affecting the accuracy of the analyses. For example, the presence of 5 percent 2,6-xylylidine in 2,4-xylylidine would cause the analysis for 2,4-xylylidine at a wavelength of 2950 Å to be 1 percent low in total amine and only 0.2 percent high at 2900 Å.

The presence of impurities in the amine blended in the fuel or, possibly, in the amine sample used in preparing the standard solution, may often be detected by discrepancies in the calculated values of amine concentration in the sample. In the procedure described, three values of c are calculated from the measured extinctions at the three different wavelengths. Variations among these three values of c greater than $\pm 1/2$ percent for a single sample indicate that the aromatic amine (or aromatic amine mixture) in the blended fuel may not be identical with the amine sample used to determine the specific extinctions.

Photochemical Decomposition of Aromatic Amines

Tests at the Cleveland laboratory have shown that the aromatic amines are unaffected by infrared and visible radiation, but ultraviolet radiation from a quartz mercury-arc lamp induces distinct

changes in the absorption characteristics of aromatic amines in hydrocarbon solutions. Because the ultraviolet radiation of the mercury-arc lamp was many times more intense than that of sunlight, it appears that the aromatic amines would not be seriously affected during a short exposure to sunlight in transferring a fuel sample from one container to another. It appears, however, that the amine determination of a fuel sample that has been stored in a glass bottle and exposed to sunlight for considerable time might be seriously in error because of the effect of the light on the absorption characteristics of the aromatic amine. Fuel samples which are to be stored before analysis must therefore be protected from exposure to strong light by storing them in lightproof containers.

The results of reference 4 also show that the ultraviolet light in the spectrophotometer is not sufficiently intense to affect the extinction measurements of the aromatic amines by as much as 1/2 percent, provided that the measurements are completed within 10 minutes. These results indicate, however, the desirability of measuring the extinctions of the solutions quickly and systematically.

Composition of Fuel

The absorption spectra of an aromatic amine may be modified by the solvent used (see reference 4). Solutions of aromatic amines measured with the spectrophotometer are generally very dilute isooctane solutions containing only relatively small amounts of the hydrocarbons composing the fuel sample. The magnitude of the effect of the composition of the original amine-blended fuel on the precision of the analyses was studied. Four fuel components - isooctane, cyclohexane, toluene, and diisobutylene - representing the four typical classes of hydrocarbons (paraffins, naphthenes, aromatics, and olefins) and a typical aviation fuel, AN-F-28, containing tetraethyl lead, dyes, and inhibitor, were used to prepare blends having about 1 percent by volume of an aromatic amine mixture. The specific extinctions of the aromatic amine mixture in each of the five solutions were determined at intervals of 25 Å in the range from 2800 to 3000 Å by the procedure previously described. Results of two independent tests are given in tables 2 and 3 for two aromatic amine mixtures of different composition. The average deviation between calculated means of the specific extinctions at nine wavelengths for the amine mixtures in the five solvents was less than 1/2 percent.

The accuracy of the analysis may also be affected by ultraviolet-absorbing contaminants in the fuel that can be extracted by hydrochloric acid, such as phenolic oxidation inhibitors, tetraethyl lead, and ethyl-fluid dye. The occurrence of such compounds in aviation gasoline in sufficient quantity to affect the measured extinctions

of the aromatic amine at the 500-fold dilution usually used in analysis is extremely unlikely and their effect on the results is in most cases insignificant. The foregoing results show that the presence of ethyl fluid, for example, has little or no effect on the results obtained.

Temperature and Evaporation

The effect of temperature on the analyses was not investigated. The results reported were obtained in a room with the temperature approximately constant at about 25° C. The effect of varying temperature on the analyses cannot be disregarded for not only would differences of 5° C in the temperature cause errors of about 1/2 percent in the volumetric measurement of the isooctane, but temperature changes also generally affect absorption spectra (reference 7).

No difficulties were observed as a result of evaporation of the isooctane solvent during the 3 to 5 minutes required for the measurement of each sample, although no covers were used on the absorption cells. In this respect, isooctane because of its higher boiling point has a decided advantage over hexane or other lighter hydrocarbons.

TESTS OF PRECISION

The precision discussed in this section is the reproducibility of the results of analyses for an aromatic amine relative to the same amine as a standard. In order to test the precision of the analytical technique two series of tests were made, one involving the analysis of a single aromatic amine in a single type of fuel stock and the other involving the analysis of aromatic amine mixtures in various types of hydrocarbon fuel. The results of such tests should indicate the precision that may be expected in the analysis of aromatic amines under different circumstances, because the first tests favor good precision whereas the second tests present conditions more unfavorable to good reproducibility.

For the first tests a series of 12 samples of fuel containing weighed amounts of a sample of *p*-cumidine (*p*-isopropylaniline) was prepared. The gasoline used contained approximately 12 percent aromatics and about 1.0 milliliter of tetraethyl lead per gallon. The *p*-cumidine concentration in each sample was about 0.36 percent by weight. The samples were analyzed with the spectrophotometer by the procedure given in this report. One of the prepared samples was arbitrarily chosen as a standard sample and the analyses of the

others were based on the specific extinctions calculated for the standard sample at three wavelengths. The concentrations of each sample, calculated from the extinctions at each of the three wavelengths, are given in table 4. The percentage deviations between the weighed and the spectrophotometrically determined amine concentrations are listed. The mean deviation was about 1/3 percent.

The data illustrating the second series of tests are given in tables 2 and 3 but are presented in table 5 in a different form as a study of the precision of the method under unfavorable analytical circumstances. The data for an amine-toluene blend were used in each set of analyses to determine the specific extinctions of the amine mixtures. The concentrations of amine mixtures in the other samples were calculated at three wavelengths across the peak of the absorption curve for each mixture. The mean deviation between the weighed and the spectrophotometrically determined concentrations was slightly greater than 0.4 percent.

The precision of routine analyses of an aromatic amine in concentrations up to 3 percent by volume in a single type of fuel stock may be expected to lie between the values given in the two groups of tests described. The test results show an average deviation of less than 0.5 percent and no errors as large as 1.0 percent.

CONCLUDING REMARKS

Ultraviolet spectrophotometric techniques were found to be applicable to the quantitative analysis for individual aromatic amines and known mixtures of aromatic amines in aviation fuels. As an example, typical hydrocarbon and gasoline solutions containing monoaryl amines in concentrations from 0.4 to 1.7 percent by weight were analyzed spectrophotometrically and results accurate, on the average, to within ± 0.5 percent of the amine were obtained. The identity of the aromatic amines in the fuel must be known.

In principle, the absolute accuracy of the spectrophotometric method is dependent upon the purity of a standard amine sample used for calibration purposes and also upon the extent of contamination of the fuel with other substances which absorb light in the region from 3050 to 2800 Å and which are extracted along with the amine by aqueous hydrochloric acid.

The analysis of the aromatic amine content of hydrocarbon fuels as tested experimentally was not affected either by the type of hydrocarbon in the fuel or by ethyl fluid in the amounts usually present in aviation fuel.

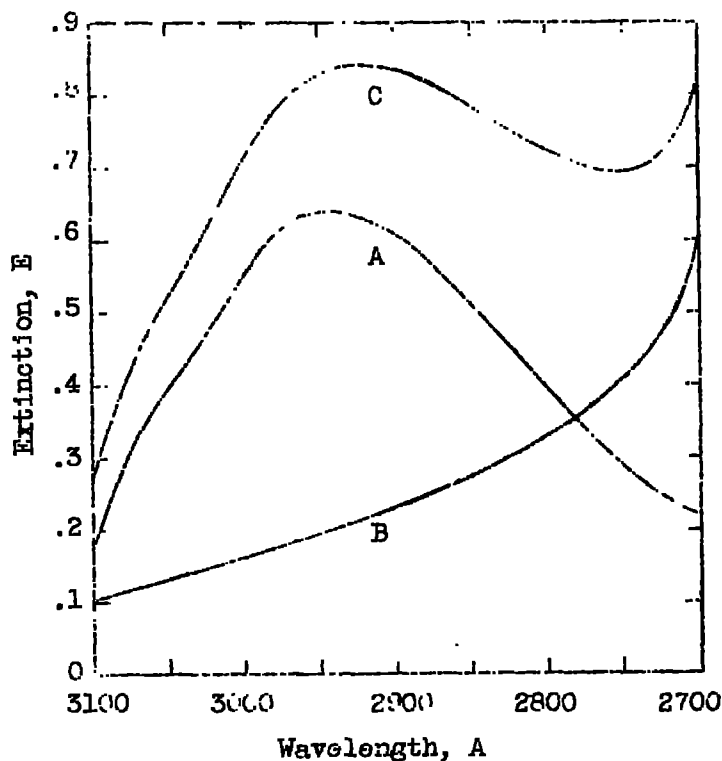
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APPENDIX A

PRINCIPLE OF ELIMINATING INTERFERENCE BY
ULTRAVIOLET-ABSORBING HYDROCARBONS

The principle of the spectrometric method for quantitative analysis of aromatic amines in the presence of hydrocarbons that also absorb ultraviolet light may be illustrated by discussing the absorption of an assumed hydrocarbon fuel containing an aromatic amine. For example, consider a fuel blend that has 3 percent of an aromatic amine (N-methylaniline) and 30 percent of ultraviolet-absorbing substances typical of those found in hydrocarbon fuels. These substances are primarily aromatics and olefins and, if the fuel is leaded, will include the tetraethyl lead and ethyl dye in the ethyl fluid. According to the procedure reported, 1 gram of the hypothetical fuel sample should be diluted with iso-octane to 1 liter or the equivalent dilution made.

The absorption spectrum - extinction plotted against wavelength - for the aromatic amine, as determined for the diluted fuel sample relative to an ultraviolet-light-transparent solvent, may be represented by curve A in the following figure:



The absorption spectrum of the ultraviolet-absorbing substances in the same solution may be represented by curve B. (In general, aromatics absorb about one-tenth as much in the region of 2750 to 2300 A as do equal amounts of aromatic amines in the region of 3050 to 2800 A; olefins absorb much less; the absorption by the ethyl-fluid dye and other components would probably be entirely negligible at the 700-fold dilution.) Because optical extinctions are additive, the resultant absorption of the diluted hypothetical fuel sample will be curve C.

When the aromatic amine is extracted from part of the fuel sample with aqueous acid, the absorption of the solution from which the amine was removed corresponds to curve B. When the extinction of the unextracted solutions is measured relative to the extracted solution at any wavelength using absorption cells of matched length, the extinction of the aromatic amine in the fuel can be measured; the aromatic amine, therefore, can be determined directly in spite of the presence of aromatics and olefins.

APPENDIX B

WAVELENGTHS USED FOR ANALYSIS AND SPECIFIC-EXTINCTION DATA

FOR 27 AROMATIC AMINES IN ISOOCTANE

Sets of three wavelengths used for the quantitative analysis of each of 27 aromatic amines in fuels and the specific extinctions for each amine taken from the curves of reference 4 are listed in table 6. The three wavelengths arbitrarily chosen lie at approximately 25 Å intervals near the absorption-band maximum for each aromatic amine.

The quartz-prism ultraviolet spectrophotometer was used to obtain these data. The slit widths were adjusted to 0.3 millimeter. The temperature of the aromatic amine solutions was approximately 25° C. The simple aromatic amines were better than 99 percent pure; the purity of aromatic amines from which isomers are difficult to separate was less; most of the aromatic amines listed were better than 95 percent pure.

The extinction data listed are not recommended for use as accurate standards for analysis purposes because other spectrophotometers may yield different specific extinctions for the same aromatic amine owing to differences in the resolution of other instruments, as well as differences in the amount of stray light. For example, with the quartz-prism spectrophotometer, a specific extinction of 17.2 liters per gram-centimeter was obtained for p-toluidine in isooctane at 2930 Å, whereas a value of 13.4 liters per gram-centimeter was obtained at this laboratory with a 1.5-meter concave-grating spectrograph using photographic techniques. The list may be used, however, as a guide for the selection of appropriate wavelength settings for the analysis of individual aromatic amines and for approximate estimations (± 10 percent) of the magnitude of absorption for an amine.

The data are grouped in families of structurally related aromatic amines. Related compounds will be observed to have their maximum absorption at approximately the same wavelength.

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TABLE 1. - PRECISION OF SPECTROPHOTOMETRIC MEASUREMENT OF
EXTINCTION - VALIDITY OF BEER-LAMBERT RELATIONSHIP

Concentration of technical xylidines in isooctane (gram/liter)	Ratio of xylidine concentration	Wavelength, A					
		2925		2900		2875	
		E_{λ}	k	E_{λ}	k	E_{λ}	k
0.00996	1	0.165	16.57	0.171	17.18	0.1685	16.92
.01992	2	.332	16.68	.343	17.23	.338	16.97
.03984	4	.660	16.58	.684	17.18	.6745	17.05
.0498	5	.826	16.60	.860	17.28	.8455	16.99
.0996	10	1.584	15.90	1.631	16.39	1.603	16.10
Average value of k for E_{λ} values less than 1.0		-----	16.61	-----	17.22	-----	16.98
Mean deviation of k from average for E_{λ} values less than 1.0, percent		-----	0.26	-----	0.22	-----	0.22

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TABLE 2. - EFFECT OF FUEL COMPOSITION ON SPECIFIC EXTINCTIONS OF AROMATIC AMINE MIXTURE 1

[Aromatic amine mixture 1 consisted of approximately equal weights of the following aromatic amines: N-ethylaniline; N,N-diethylaniline; N-butyraniline; o-toluidine.]

Wave-length (A)	Solvent ^a					Average k_{λ}	Mean deviation of k_{λ} values from average k_{λ} (percent)
	Isooctane	Cyclohexane	Toluene	Diisobutylene	AN-F-28 fuel		
	Original concentration of amine mixture in solvent, percent by weight						
	1.712	1.417	1.246	1.662	1.595		
	Specific extinctions, k_{λ}						
2800	11.86	11.71	11.87	12.11	11.96	11.91	0.94
2825	13.21	13.27	13.23	13.32	13.33	13.27	.30
2850	14.54	14.59	14.54	14.56	14.63	14.57	.21
2875	15.52	15.65	15.51	15.54	15.75	15.59	.54
2900	16.03	16.20	16.11	16.10	16.22	16.13	.38
2925	16.20	16.28	16.26	16.25	16.33	16.26	.18
2950	15.90	16.02	15.96	15.90	16.08	15.97	.39
2975	14.85	15.03	14.87	15.00	14.99	14.95	.47
3000	13.22	13.30	13.26	13.39	13.30	13.29	.33
Average	-----	-----	-----	-----	-----	-----	.42

^aIsooctane solvent was S-3 reference fuel; S-3 reference fuel was used in making all dilutions. Cyclohexane, toluene, and diisobutylene were technical products. AN-F-28 fuel is grade 100/130 aviation fuel.

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TABLE 3. - EFFECT OF FUEL COMPOSITION ON SPECIFIC EXTINCTIONS OF AROMATIC AMINE MIXTURE 2

[Aromatic amine mixture 2 consisted of equal volumes at 25° C of the following aromatic amines: N-ethylaniline; N,N-diethylaniline; N-butaniline; o-toluidine; carvacrylamine (5-isopropyl-2-methylaniline).]

Wave-length (A)	Solvent ^a					Average k_{λ}	Mean deviation of k_{λ} values from average k_{λ} (percent)
	Isooctane	Cyclohexane	Toluene	Diisobutylene	AN-F-28 fuel		
	Original concentration of amine mixture in solvent, percent by weight						
	1.617	1.419	1.274	1.531	1.554		
	Specific extinctions, k_{λ}						
2800	12.42	12.42	12.40	12.60	12.46	12.46	0.45
2825	13.86	13.88	13.90	14.04	13.80	13.90	.43
2850	15.20	15.25	15.15	15.35	15.19	15.23	.38
2875	16.06	16.14	16.03	16.13	15.98	16.07	.35
2900	16.38	16.50	16.35	16.35	16.31	16.38	.31
2925	16.20	16.25	16.14	16.20	16.05	16.17	.36
2950	15.52	15.58	15.45	15.58	15.40	15.51	.41
2975	13.86	14.04	13.86	13.96	13.84	13.91	.50
3000	11.74	11.84	11.79	11.98	11.70	11.81	.69
Average	-----	-----	-----	-----	-----	-----	.44

^aIsooctane solvent was S-3 reference fuel; S-3 reference fuel was used in making all dilutions. Cyclohexane, toluene, and diisobutylene were technical products. AN-F-28 fuel is grade 100/130 aviation fuel.

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TABLE 4. - ANALYTICAL PRECISION FOR p-CUMIDINE
IN TYPICAL FUEL BLEND

Weighed concentration of amine in prepared solution (percent by weight)	Concentrations determined spectrophotometrically at each of three wavelengths (percent by weight)			Average experimentally determined concentration (percent by weight)	Deviation between weighed and determined concentration (percent)
	Wavelength, λ (A)				
	2900	2925	2950		
0.3636	0.364	0.364	0.364	0.3640	0.11
.3596	.358	.358	.358	.3580	.45
.3468	.349	.349	.349	.3490	.63
.3788	.380	.380	.379	.3793	.13
.3700	.372	.372	.370	.3713	.35
.3704	.369	.369	.368	.3687	.46
.3652	.365	.365	.365	.3650	.05
.3920	.390	.391	.390	.3903	.43
.3528	.354	.355	.352	.3537	.26
.3748	.373	.373	.373	.3730	.48
.3628	.361	.361	.359	.3603	.41
Mean deviation, percent	-----	-----	-----	-----	.34

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TABLE 5. - ANALYTICAL PRECISION FOR AROMATIC AMINE MIXTURES IN VARIOUS HYDROCARBON SOLVENTS

	Weighed concentration of amine in prepared solution (percent by weight)	Concentration ^a determined spectrophotometrically at different wavelengths (percent by weight)				Average experimentally determined concentration (percent by weight)	Deviation between weighed and determined concentration (percent)
		Wavelength, λ (Å)					
		2875	2930	2925	2950		
Aromatic amine mixture 1 ^b in various hydrocarbon solvents:							
Isooctane	1.712	-----	1.721	1.719	1.719	1.720	0.47
Cyclohexane	1.418	-----	1.410	1.416	1.413	1.413	.35
Diisobutylene	1.662	-----	1.660	1.663	1.668	1.665	.18
AN-F-28 fuel	1.595	-----	1.584	1.588	1.584	1.586	.56
Aromatic amine mixture 2 ^c in various hydrocarbon solvents:							
Isooctane	1.617	1.614	1.614	1.611	-----	1.613	0.25
Cyclohexane	1.419	1.409	1.406	1.409	-----	1.408	.78
Diisobutylene	1.531	1.521	1.531	1.525	-----	1.526	.33
AN-F-28 fuel	1.554	1.559	1.558	1.563	-----	1.560	.39
Mean deviation, percent	-----	-----	-----	-----	-----	-----	0.41

^aCalculation of concentrations based on specific extinctions for aromatic amine mixture blended with toluene and diluted with isooctane.

^bAromatic amine mixture 1 consisted of approximately equal weights of the following aromatic amines: N-ethylaniline; N,N-diethylaniline; N-butaniline; o-toluidine.

^cAromatic amine mixture 2 consisted of equal volumes at 25° C of the following aromatic amines: N-ethylaniline; N,N-diethylaniline; N-butaniline; o-toluidine; carvacrylamine.

TABLE 6. - WAVELENGTHS USED FOR ANALYSIS AND SPECIFIC-EXTINCTION VALUES

FOR 27 AROMATIC AMINES IN ISOOCTANE

[Beckman quartz-prism spectrophotometer Model DU; slit width, 0.3 millimeter; hydrogen discharge lamp; absorption-cell length, 1 centimeter; concentrations of aromatic amine in isooctane, about 0.05 gram per liter]

Aromatic amine	1		2		3	
	Wave-length λ (A)	^a Specific extinction k_{λ} (liters/gram-cm)	Wave-length λ (A)	^a Specific extinction k_{λ} (liters/gram-cm)	Wave-length λ (A)	^a Specific extinction k_{λ} (liters/gram-cm)
^b Aniline	2840	18.5	2880	19.0	2920	16.7
^b N-Methylaniline	2925	21.0	2950	21.3	2975	20.4
^b N-Ethylaniline	2925	18.0	2950	18.3	2975	17.9
N-Propylaniline	2925	15.7	2950	16.1	2975	16.0
N-Isopropylaniline	2925	14.9	2950	15.2	2975	15.0
^b N-Butylaniline	2925	14.3	2950	14.7	2975	14.4
N- <u>tert</u> -Butylaniline	2925	10.4	2950	10.4	2975	10.2
^b N,N-Dimethylaniline	2950	18.7	2975	19.0	3000	18.8
N,N-Diethylaniline	3000	16.0	3025	16.2	3050	15.7
^b <u>o</u> -Toluidine	2850	20.9	2875	20.2	2900	18.8
^b <u>o</u> -Ethylaniline	2850	18.5	2875	18.4	2900	17.2
<u>o</u> -Isopropylaniline	2850	16.9	2875	17.0	2900	15.9
^b <u>m</u> -Toluidine	2850	16.3	2875	17.0	2900	16.8
^b <u>p</u> -Toluidine	2900	16.5	2930	17.2	2960	16.9
^b <u>p</u> -Ethylaniline	2900	14.5	2925	15.1	2950	14.8
<u>p</u> -Isopropylaniline	2900	13.6	2925	13.7	2950	13.2
<u>p</u> - <u>tert</u> -Butylaniline	2875	11.7	2900	11.9	2925	11.7
N-Methyl- <u>p</u> -toluidine	2975	17.3	3000	17.6	3025	17.6
N-Ethyl- <u>p</u> -toluidine	3000	15.6	3025	15.9	3050	15.4
N-Isopropyl- <u>p</u> -toluidine	3000	13.4	3025	13.7	3050	13.6
2,4-Xylidine	2900	18.6	2925	19.1	2950	18.6
2,4-Diethylaniline	2900	15.2	2925	15.4	2950	14.7
2,5-Xylidine	2850	19.3	2975	19.9	2900	19.6
2,6-Xylidine	2850	17.2	2875	17.9	2900	17.8
Xylidines, technical	2875	17.0	2900	17.2	2925	16.6
N-Methyl-2,4-xylidine	2950	18.8	2975	19.3	3000	18.9
Mesidine	2875	17.5	2900	18.0	2925	17.8

^aThe values of k_{λ} are rounded off to three significant figures.

^bThese aromatic amines were better than 99 percent pure

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